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**A STUDY OF CHEMICAL REACTIONS AND INTERACTIONS IN MICROEMULSION
AND SURFACTANT PHASES.**

BY

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We have carried out a variety of chemical and physical studies in microemulsions phases formed from water, surfactant, oil, and an alcohol cosurfactant. These are isotropic, stable, clear phases of low viscosity. Most of the work was performed in oil in water microemulsions consisting of oil droplets in an aqueous continuous phase. Cationic, anionic and nonionic surfactants have been employed. From transport measurements we have examined the location of solutes, their diffusion rates, and degree of counterion dissociation in ionic systems. | | |

An electro chemical method for the determination of droplet size has been developed. From kinetic studies of phosphate ester-nucleophile reactions, a quantitative ion-exchange model has been developed. This model has been shown to be consistent with both the kinetic data and acid-base indicator equilibrium data. Surface bound aldoxinate nucleophile has been shown to be more effective than hydroxide in ester hydrolysis. Other reactions of inorganic ions have also been examined, and borohydride ion has been shown to react with chloroethyl ethyl sulfide in a cationic microemulsion. These results clearly demonstrate the utility of microemulsion for both fundamental studies and for application to such problems as solubilization, catalysis, and chemical decontamination.

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FORWARD

This is the final report on contract DAAG29-79-C-0089, "A study of Chemical Reactions and Interactions in Microemulsion and Surfactant Phases", covering the period May 1, 1979 to April 30, 1982. Much of the work performed during this period is published, in press, or in preparation. This report will therefore consist of a summary of the work performed with references to the published or in press material, supplemented by as yet unpublished or incomplete data where appropriate.

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I. Introduction

A. Significance and Objectives. Over the past twenty years there have been an increasing number of investigations of the effect of surfactants on the courses and rates of chemical reactions (1,2). These studies have been primarily concerned with the influence of normal micelles in aqueous solution (3), although the action of reversed micelles (4), lyotropic liquid crystalline phases (5) and vesicles (6), have also recently been examined.

Reactions in monolayers and in the presence of polyelectrolytes, which have many features related to those of reactions in micellar systems, have also been investigated (7-9). These studies have been conducted to gain additional understanding of the factors which influence the courses and rates of chemical reactions and the nature of intermolecular interactions in solution. Further motivation lies in the potential utilization of these results for the purpose of organic synthesis and to provide insight into enzymatic catalysis. Common to all of these systems is the presence of microscopic "oil-water" interfaces.

Very few comparable studies have been performed in microemulsions which possess some unique differences compared with micelles, monolayers or polyelectrolytes. One of the most important properties of microemulsions is their ability to dissolve a great variety of solutes due to the wide range of polarities available in the different phases. A solute may be present in a number of environments; the oil phase; the aqueous phase; the interphase; distributed between two or three phases. Selectivity with respect to a given solute molecule can be achieved by means of the initial composition and the choice of oil and surfactant.

An aqueous micelle may incorporate one, or perhaps a few, solute molecules in its surface. Since a microdroplet in a micellar emulsion has a sizable

surface phase of intermediate polarity, a large number of solute molecules may aggregate in the interphase region. Very non-polar solutes will be located in the core of a micelle, while they will effectively be dissolved in the "bulk-oil" phase in an o/w microemulsion. A coarse emulsion might be expected to exhibit behavior somewhat similar to that of a microemulsion, but is polydisperse, inherently unstable and turbid.

The studies which have been conducted to date in microemulsions include metal ion incorporation by tetraphenylporphine (10,11), formation of metal complexes with amino alcohols (12,13), electrochemical (14-17) and photochemical studies (18,19), as well as acid-base (20) and hydrolysis reactions (20,21). These investigations have clearly demonstrated the great utility and yet greater potential of these media for the study of processes occurring in interfacial environments. In evidence of this, a significant number of papers dealing specifically with reactions in microemulsions have appeared in the last three years. A review article dealing with reactions in microemulsions up to 1980 has just been published (22).

The purpose of this study was to continue in depth investigations of the utility of microemulsion systems for studies of interactions at microscopic oil-waters interfaces and for possible applications to areas such as solubilization, catalysis and chemical decontamination.

B. Microemulsions. Since we have performed physicochemical investigations in microemulsion media, some initial discussion of the nature of these systems is in order. There is not universal agreement concerning both the scope and nature of the fluids which have been variously called microemulsions (23-26), solubilized micellar solutions (27), and micellar emulsions (28). All of these systems are translucent or transparent dispersions of oil in water (o/w) or water in oil (w/o) which contain one or more amphiphilic compounds and are mechanically stable. However, the crux of the problem concerning the definition of a microemulsion is whether it is thermodynamically or kinetically stable (29,30). There are some systems which are demonstrably only kinetically stable (16,17,31,32) while many others appear thermodynamically stable (10-15, 21,33). Unfortunately, it is often experimentally difficult, especially in these compositionally complex systems, to prove thermodynamic stability. In light of this, Reed and Healy (33) have employed the operational definition that a microemulsion is a "persistent translucent combination of oil and water that may contain electrolytes and one or more amphiphilic compounds". The definition of "persistent" is then left to the requirements of the specific application. The amphiphiles are normally surfactants (e.g. soaps and detergents), and frequently include cosurfactants such as alcohols. The alcohols are normally C_4 - C_{10} and are not very water soluble. However, the definition of amphiphile must include molecules which are very soluble in both oil and water since microemulsions exist which are stabilized only by isopropanol (34).

In general, the systems employed in this study are transparent rather than translucent, and are composed of relatively high amounts of emulsifier (10-40%). The emulsifier E consists of a surfactant S

and alcohol A. The aqueous component W may be pure water or may contain added salts or buffers. The oil O is a liquid which is not miscible with water such as benzene, hexadecane or mineral oil. In addition to being mechanically stable, all of these microemulsions have been subjected to thermodynamic stability tests insofar as their physical properties are concerned. Some of the criteria which were employed are listed below.

1. Their formation must be spontaneous and independent of the method or order of addition of components.
2. The value of any physical measurement (e.g. - conductivity) at a given composition must be independent of the path by which that composition is reached.
3. After being subjected to a perturbation which causes phase separation (e.g. - temperature) the system must return to its original state. Both visual and physical measurements should be employed to determine, insofar as possible, if the original state has been reproduced.

Since it is never possible to prove absolutely the single phase nature of these systems, we shall continue to discuss them using the language of emulsions. Thus, their internal structure may be described as a collection of oil or water microdroplets dispersed in water or oil, respectively. The volume occupied by the dispersed phase (phase volume) is high (e.g. 20-80%). The droplet diameter is on the order of 100-600A, and in this size range has been found to be monodisperse (24,26,35-38), although recent work has provided evidence of more complex behavior in some systems (39). The droplet itself may be conceptually divided into two regions, the oil or water core and the surface or interphase region. Essentially all of the surfactant and a part of

the alcohol cosurfactant is located in the interphase region. There is some evidence to suggest a relatively constant S/A mole ratio (35,38,40,41), but this would not normally be expected to be the case (42). A model of an o/w micellar emulsion droplet stabilized by an ionic detergent and an alcohol is shown in figure 1. Accounts of earlier work on microemulsion formation and structure may be found in reviews by Shinoda and Friberg (43) and Prince (44). An excellent survey of the literature from 1975-1979 which contains additional references supplementing the representative papers cited above has recently been published by Holt (45).

Due to the different solubility and solvation requirements of the emulsifier with respect to oil and water, there is a lack of symmetry between the o/w and w/o systems. For example, little change in radius is expected upon dilution of an o/w microemulsion with water, whereas a significant variation in size should arise by dilution of a w/o system with oil. The transition of o/w to w/o systems has been considered by a number of investigators (33,46-49). Under appropriate conditions, a third phase may be obtained which appears to be both oil and water continuous. This phase has been called the middle (33) or surfactant (43) phase. We shall use the latter designation since "middle" usually refers to a phase consisting of hexagonally close packed cylinders. It has been variously suggested that the surfactant phase consists of bicontinuous structures (49), lamellae of oil and water (50), or molecularly dispersed solutions (51).

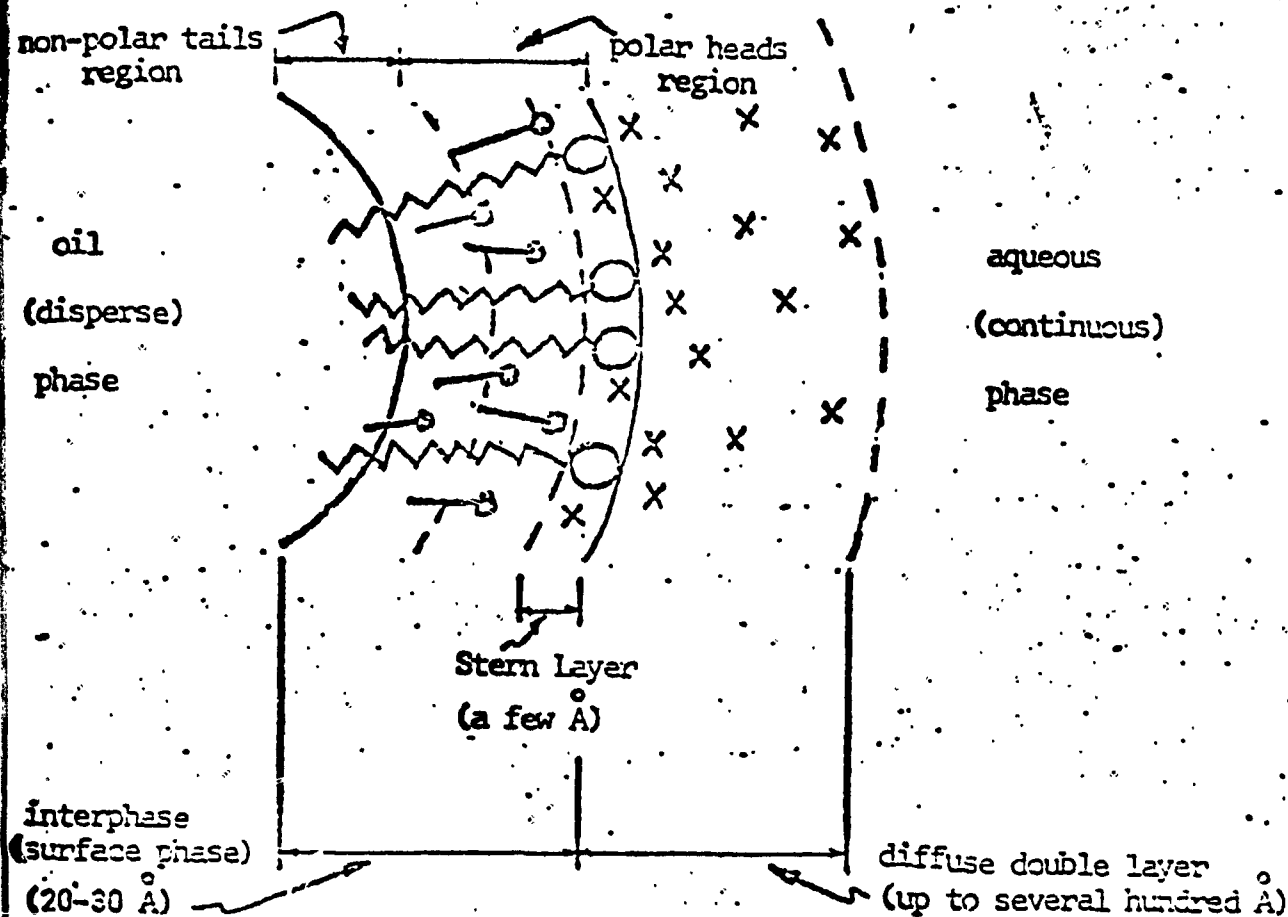


Figure 1. A model of an oil microdroplet in an O/W micellar emulsion stabilized by ionic detergent and an alcohol (C_{12}). The counterions (X), head groups (C), hydrocarb. chains (~~~~) and alcohol molecules (—o) are schematically indicated to denote their relative locations but not their number, distribution or configuration. Some alcohol is normally present in the oil phase, and both oil and water molecules can penetrate the interphase to some extent.

II. Results

As mentioned above, a number of significant publications concerning reactions in microemulsions have appeared in the past few years. While these studies have clearly shown both the potential and utility of microemulsions as reaction media, much work remains to unify this field. In particular, a wider variety of reaction systems need to be examined, in conjunction with more detailed investigations of the internal structure of the microemulsions employed. Nonetheless, it is at the same time essential to continue fundamental studies designed to model the basic aspects of these interfacial reactions. In this section I will discuss the results we have obtained to date.

A. Transport Measurements. A knowledge of the transport properties of both the microdrops and solutes in the microemulsion are necessary for the interpretation of chemical processes taking place in these media. Three important questions are (1) the location of the solute, (2) the size of the microdroplet and (3) the degree of dissociation of the counterion (for ionic systems). To address these questions, we have been employing primarily electrochemical measurements, namely conductance and polarography (14,15).

We have established criteria in both ionic and nonionic microemulsions (M.E.) for free and bound electroactive solutes. In both types of M.E. the diffusion coefficient (D) obtained from the voltammetric measurements increases with decreasing phase volume (increasing water content).

We have established an empirical relationship between D and the compositional phase volume ϕ_{comp} (52) for free species in nonionic

microemulsions given by equation 1 (15).

$$D = D_0(1 - \phi_{\text{comp}})^{n+1} \quad (1)$$

Here, D_0 is the diffusion coefficient in the continuous (e.g. - aqueous) phase and n is an exponent which is equal to 1.5 at low oil content and decreases toward the expected value of 0.5 for a classical (macro) emulsion. This is the same exponent which can be used to describe the behavior of the equivalent conductivity Λ of nonionic microemulsions containing added salt, which decreases with increasing drop size (42). Typical results are shown in figure 2. Solutes which are bound to or dissolved in the microdrop are expected to provide a measure of the droplet diffusion coefficient, which should at the least be of considerably lesser magnitude. This expectation is realized for ionic microemulsions (vide infra), but a quite different behavior is exhibited in nonionic M.E., as shown in figure 3. The value of D_0 for the drops has been calculated from the radius determined by light scattering (42). The oil soluble 1-dodecyl-4-cyanopyridinium ion has been used as the probe, and D actually decreases with increasing water content. This is reminiscent of the results of conductivity measurements in w/o microemulsions, which were ascribed to percolation phenomena (53). We have also obtained similar results with another nonionic ME stabilized by Brij 96, and the results may be quantitatively fit by the percolation and effective medium theories (54). In effect, this means that collisions between uncharged droplets in o/w microemulsions are "sticky". In any event, the distinction between free and bound species is clear.

In ionic microemulsions, droplet bound species give quite different results, which permit a determination of the droplet diffusion coefficient.

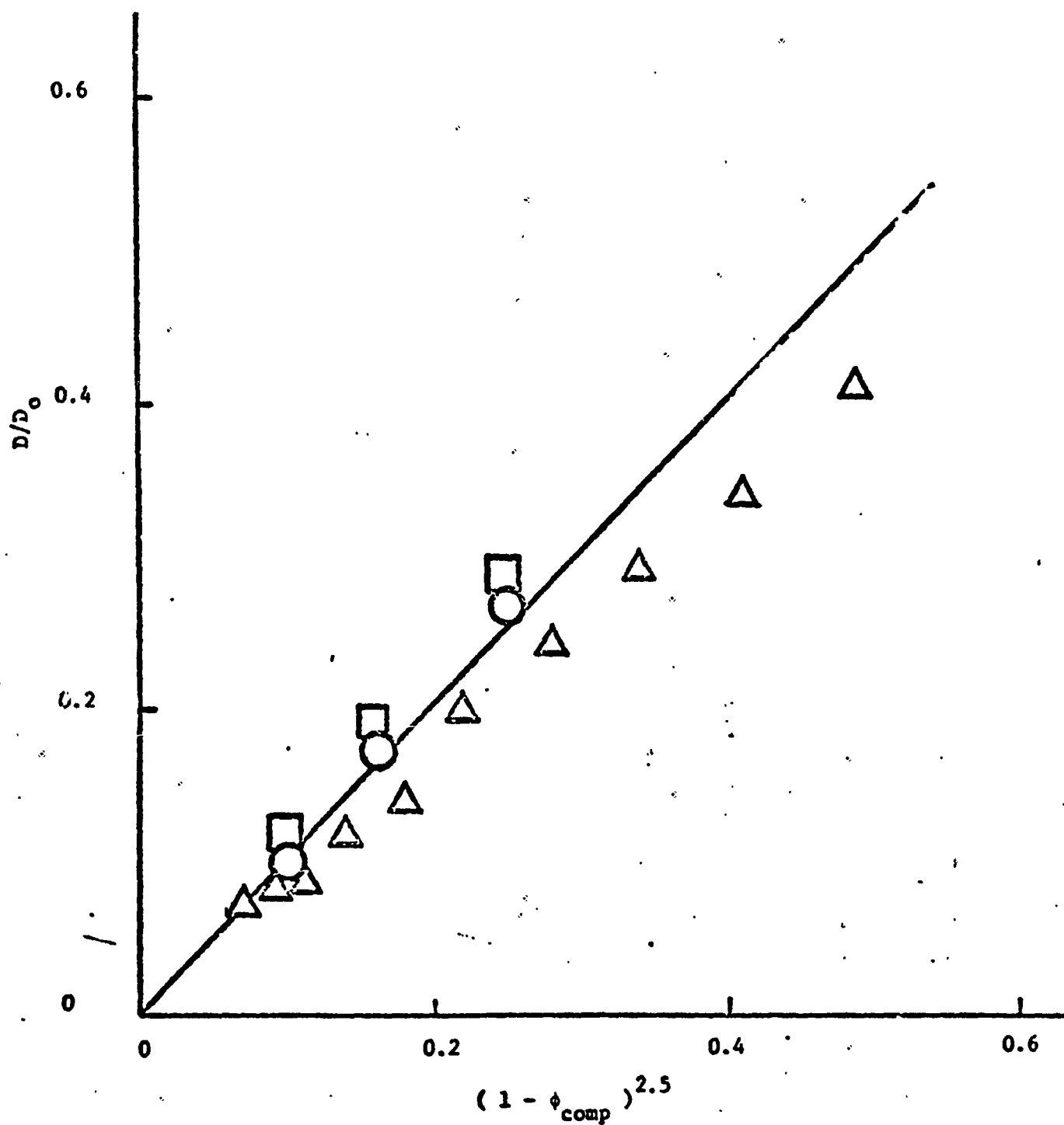


FIGURE 2. Diffusion coefficient ratio (D/D_0) for Cd(II) (triangles), Fe(CN)_6^{3-} (squares) and Fe(CN)_6^{4-} (circles) in the Tween[®] 60/1-pentanol/hexadecane (initial 7%) microemulsion vs given function of phase volume (vide text). Solid line is 45° line.

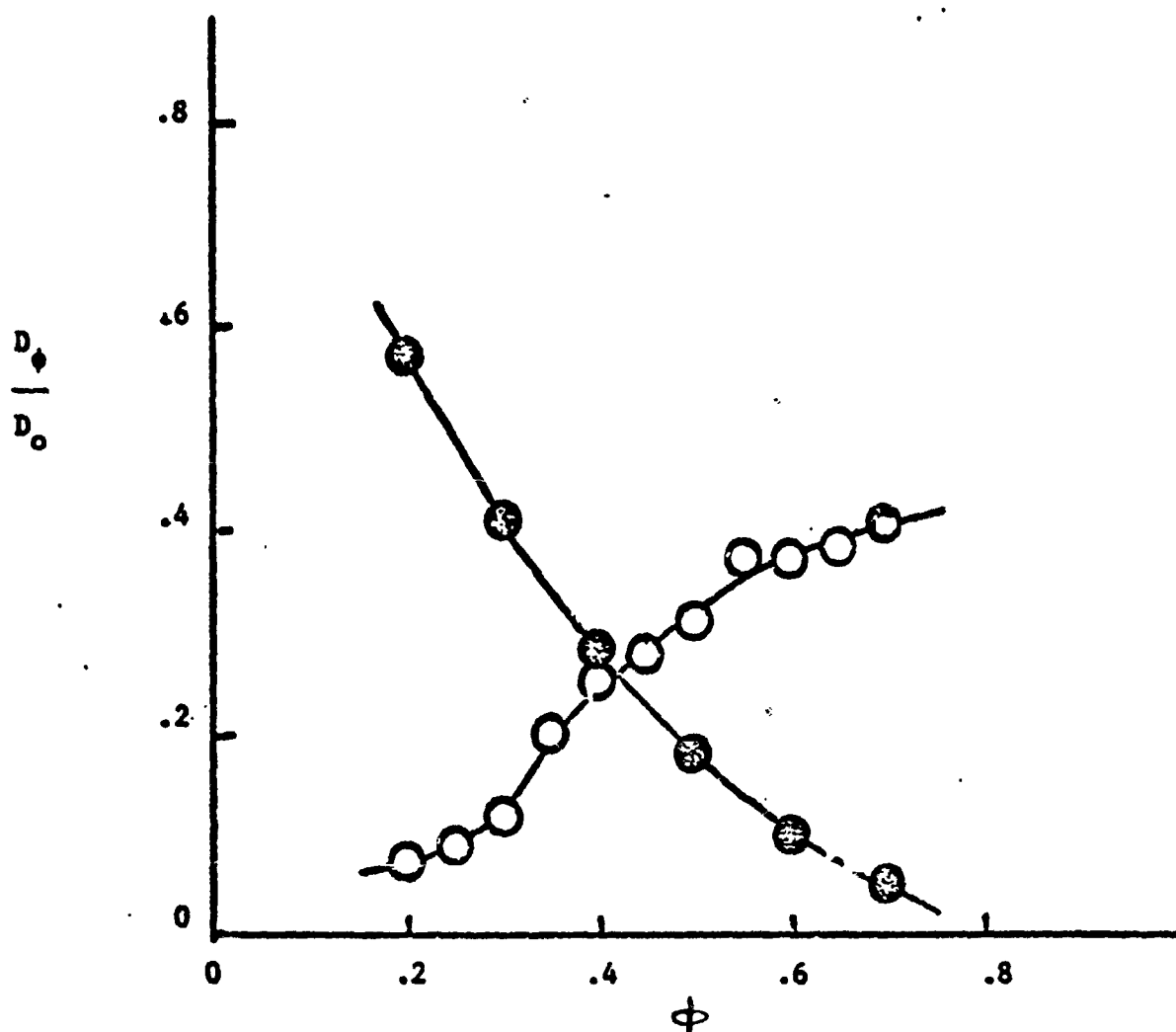


Figure 3. Ratio of diffusion coefficient in a nonionic Tween 60/pentanol/hexadecane (7% initial w/w) o/w microemulsion (D_ϕ) to that in water (D_0) for droplets (open circles) and aqueous ions (closed circles).

The value of D is found to be essentially constant over the range $.3 < \phi < .7$, regardless of the system. For example, in a mineral oil in water microemulsion stabilized by sodium cetyl sulfate (SCS) and 1-pentanol as cosurfactant (20), a value of $D = 4.2 \pm 0.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ is obtained. In a hexadecane in water system containing cetyltrimethylammonium bromide (CTAB) and 1-butanol (21), $D = 7.3 \pm 0.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (55). From the Stokes-Einstein equation (eqn. 2), a radius r can be calculated.

$$D = kT/6 \pi r \eta \quad (2)$$

Here, k , T and η are the Boltzman Constant, absolute temperature, and continuous phase viscosity, respectively. The values of r thus obtained are quite reasonable. Other methods of size determination exist, including light scattering, small angle x-ray, neutron scattering, and fluorescence quenching. All of these suffer from some degree of difficulty, and in some cases are not of general applicability. Little confirmed size data exist, particularly for o/w systems. However, the limited comparison shown in table 1 indicates that the method is valid. We have also obtained other evidence consistent with this interpretation of the data. For example, all species which are bound should exhibit the same behavior and give the same value of D , as illustrated by data for the $\text{Fe}(\text{CN})_6^{3-}$ ion in a cationic (CTAB) microemulsion shown in figure 4. A value of $r = 30 \pm 3 \text{ \AA}$ is obtained, compared with the value of $33 \pm 2 \text{ \AA}$ from pyridinium ion (Table 1). It is also clear from figure 4 that free ions, such as $\text{Fe}(\text{CN})_6^{3-}$ in an anionic M.E., behave as do free ions in nonionic M.E.

It may be noted that the same results are also obtained using n -alkyl pyridinium and viologen ions. The solubility can be varied from

completely water soluble to completely oil soluble by varying the chain length, as shown in figure 5. For $n > 8$, the probe is completely incorporated in the drop. The partition coefficient of the intermediate chain lengths ($2 < n < 8$) may also be obtained from this data (58).

Table 1. Comparison of Droplet Radii Obtained by Different Methods.

| Microemulsion System | Radius (Å) | | | |
|---|---------------------|-------------------|------------------|-----------------|
| | POL. ^{e,f} | SAXS ^e | QLS ^e | FQ ^e |
| SCS/MO/PeOH ^a | 58 | 50 ^f | --- | --- |
| CTAB/HD/BuOH ^b | 33 | --- | 34 ^f | --- |
| SDS/DD/PeOH ^c (composition A) | 34 | --- | --- | 37 ^g |
| SDS/DD/PeOH ^d (composition B) | 41 | | | 40 ^h |

- a. 60% water, 21% mineral oil initial (see reference 20).
- b. 60% water, 10% hexadecane initial (see reference 21).
- c. Sodium dodecyl sulfate (SDS), ~6%, dodecane (DD) ~5%, pentanol (PeOH) ~10% (see reference 56).
- d. SDS ~14%, DD ~7%, PeOH ~9% (see reference 57).
- e. Method employed: Polarography (POL), Small Angle X-ray Scattering (SAXS), Quasi-elastic light scattering (QLS), Fluorescence Quenching (FQ).
- f. This laboratory.
- g. Quenching of Ru(bipy)₃²⁺ by 9-methylanthracene (reference 56).
- h. Pyrene excimer quenching (reference 57).

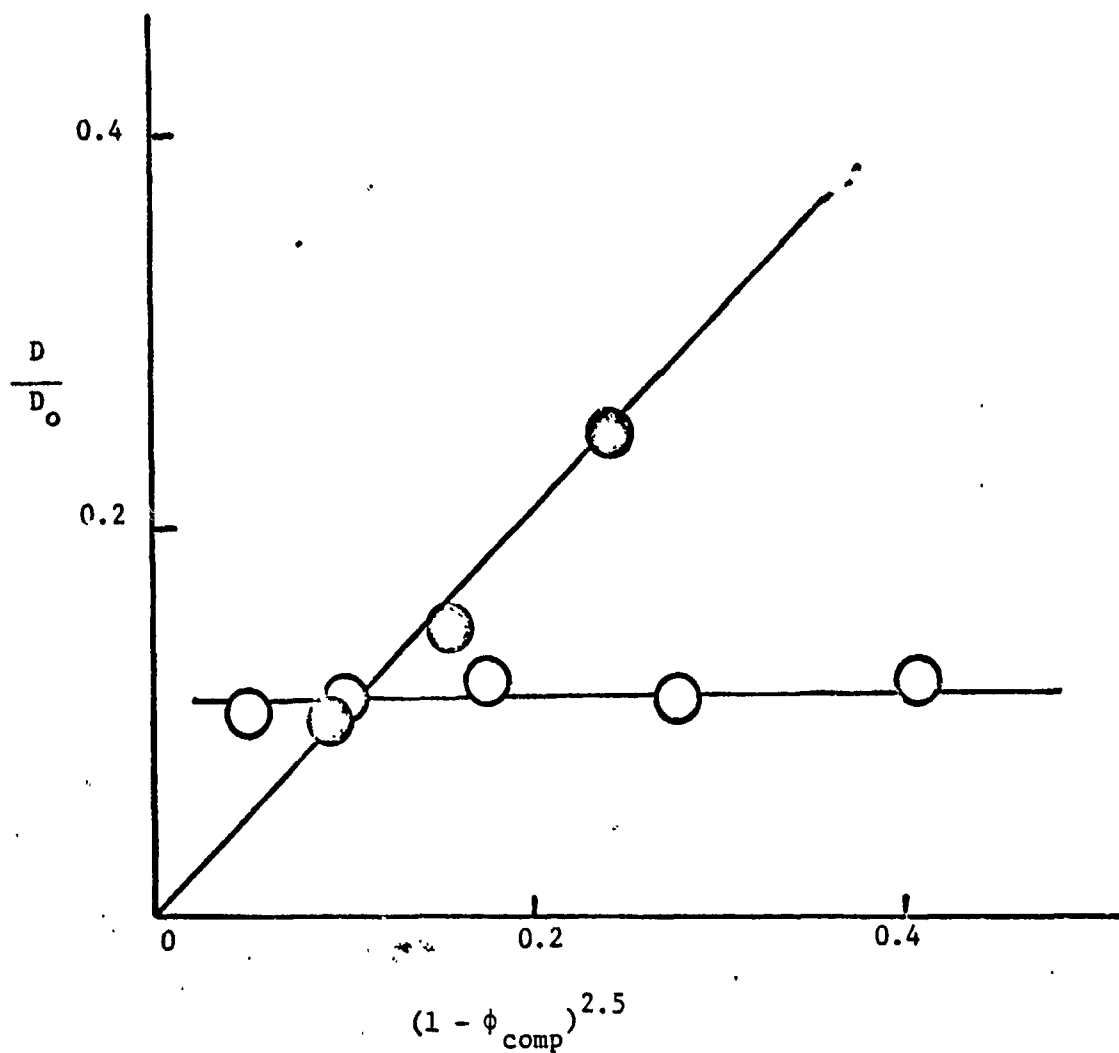


Figure 4. Diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$ in a cationic CTAB microemulsion (open circles) and an anionic SCS microemulsion (closed circles) as a function of phase volume (vide text).

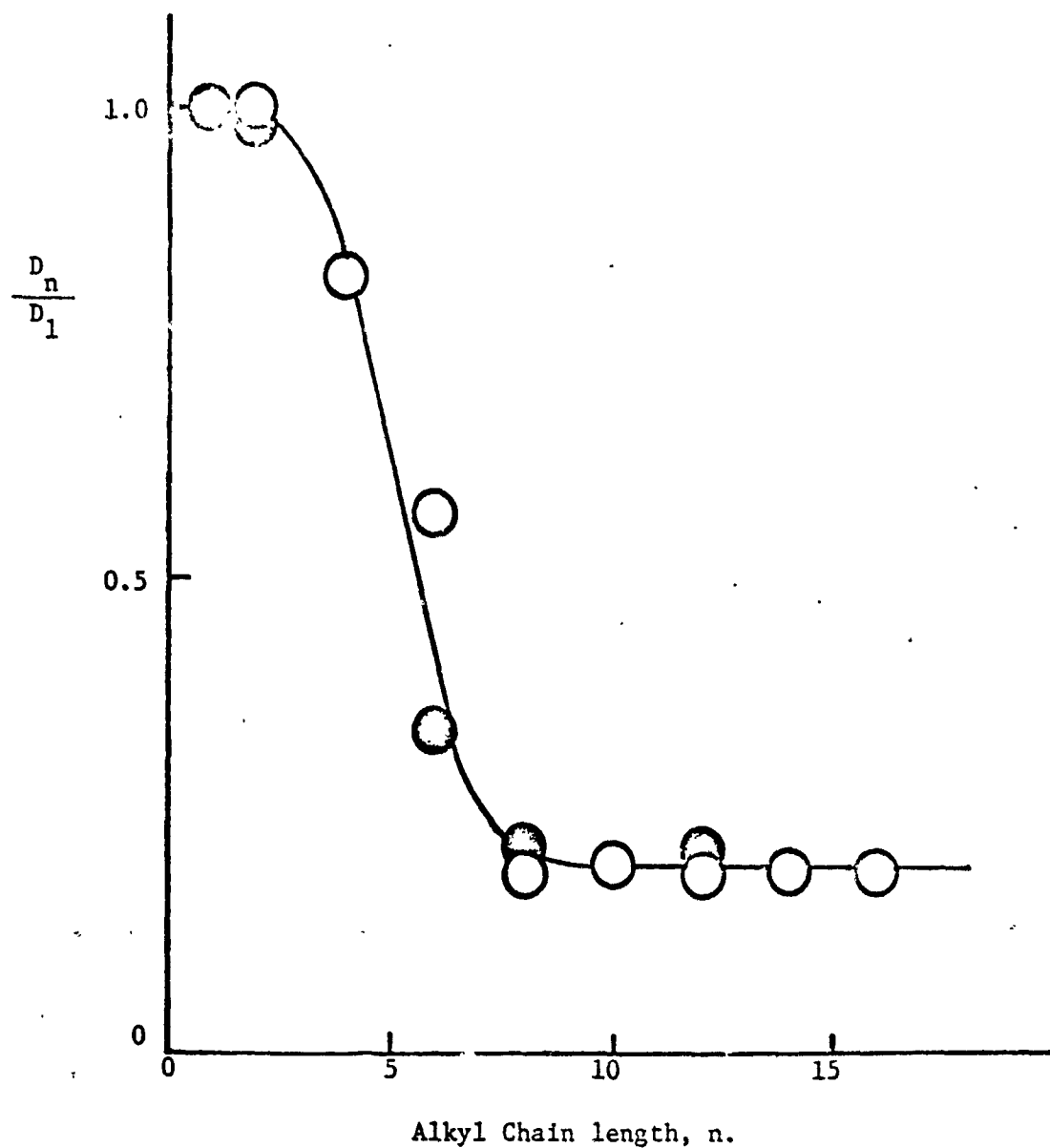


Figure 5. Diffusion coefficient of n-alkyl pyridinium (open circles) and viologen (closed circles) ions, normalized to $n = 1$, as a function of alkyl chain length n for a SCS/mineral oil/1-pentanol microemulsion of $\phi_{\text{comp}} = 0.4$.

As mentioned above, we have also performed conductivity measurements in both ionic (20) and nonionic (15) microemulsions. For the latter, the data were fit semi-empirically assuming that a constant 20% of the droplet phase volume was "interfacial" water (e.g. - water of hydration of the ethylene oxide groups, dissolved water, etc.). Recent dielectric measurements have confirmed this qualitative picture, but indicate that the amount of interfacial water depends on ϕ (59).

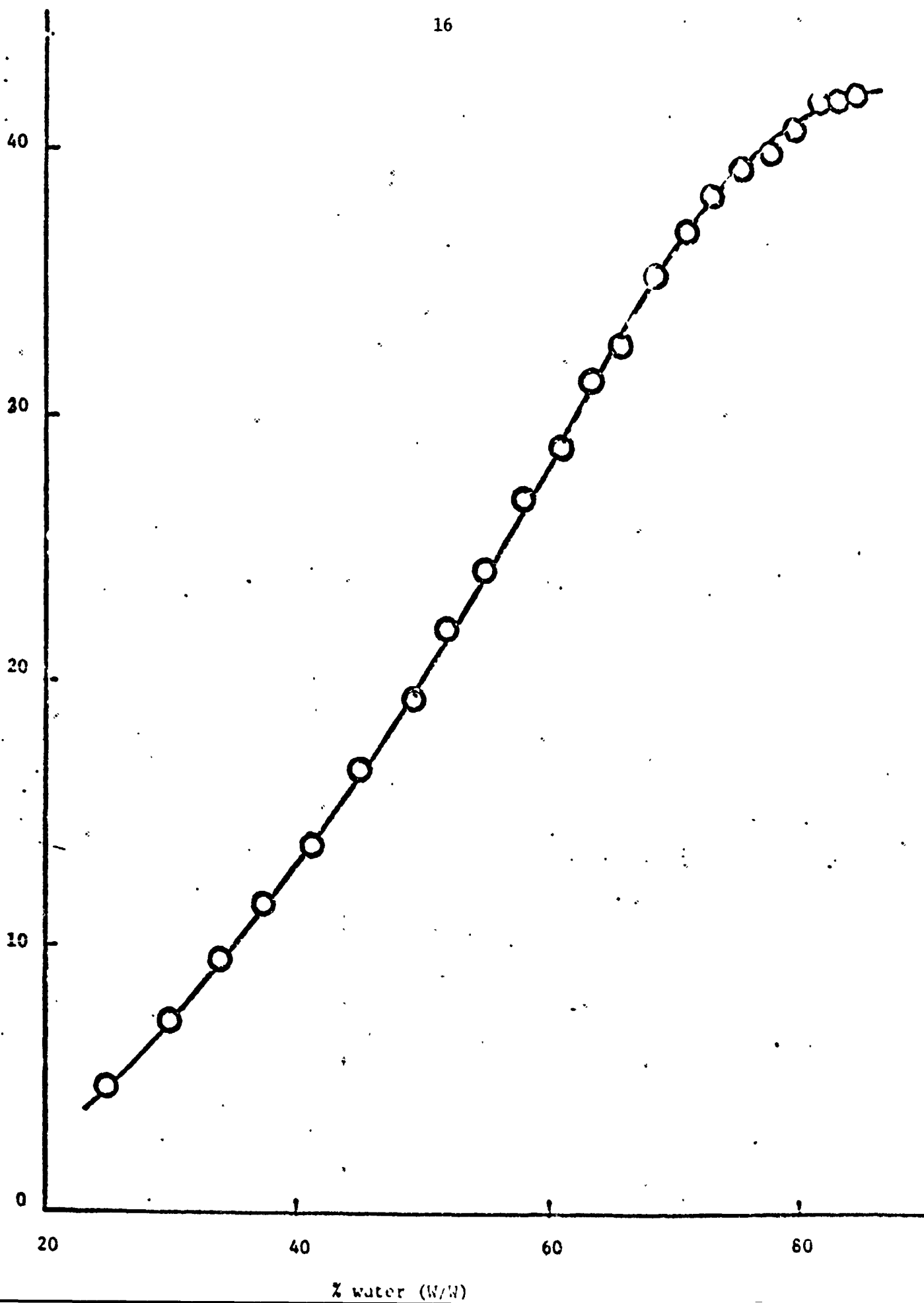
We have recently interpreted the former data on the basis of counterion dissociation and simple electrolyte theory (55,58). If the degree of dissociation is α , then Λ is given by equation 3,

$$\Lambda = (\lambda_1 + \lambda_2) \alpha \quad (3)$$

where λ_1 and λ_2 are the equivalent conductivities of the counterion and drop respectively. Equation (4) then follows from equation (2) and the relation between D_1 and λ_1 .

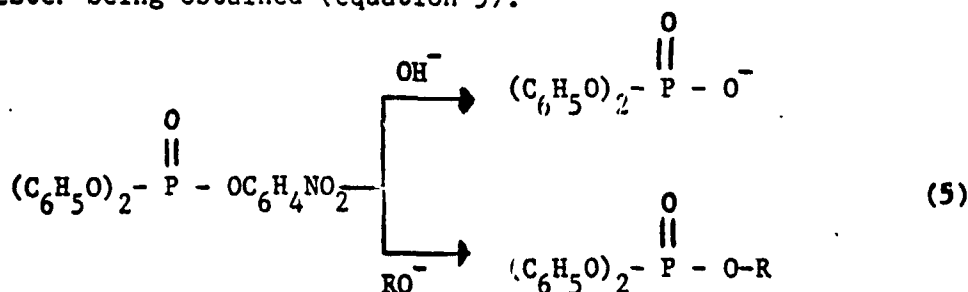
$$F^2/RT(\alpha)^2 + \lambda_1/z_2 D_2(\alpha) - \Lambda/z_2 D_2 = 0 \quad (4)$$

Here, R , F , z_2 , and D_2 are the gas constant, Faraday, number of (ionic) surfactant molecules per drop, and the droplet diffusion coefficient, respectively. The value of z_2 may be obtained from the drop radius (r), which may be either independently determined or calculated from the (polarographically) measured value of D_2 . Conductivity data for the SCS/mineral oil/1-pentanol M.E. are shown in figure 6. Values of α obtained from the combined conductance and plarography data via equation (4) in the SCS system range from $\alpha = 0.05 - 0.20$ for $\phi_{\text{comp}} = .80 - .20$. The values are



reasonable, and as might be expected increase with increasing dilution (water content). These values are somewhat lower than those generally determined for aqueous micelles, where usually $\alpha = 0.2 - 0.4$ (60). However, further work is required to test the simple theory, or more elaborate modifications thereof. In particular, some independent means of determining α is needed, and this will be addressed again below.

B. Phosphate Ester - Nucleophile Reactions. We have investigated the reaction between (oil soluble) phosphate esters, principally p-nitrophenyldiphenylphosphate (PhP), with aqueous hydroxide and fluoride ion in both cationic (CTAB) and nonionic (Brij 96) microemulsions (21,61). Some measurements have also been performed in mixed CTAB-Brij systems, and all of the results compared with those obtained in simple aqueous micelles. The rate constants and activation enthalpies (ΔH^\ddagger) we obtained in aqueous CTAB micelles agreed with those reported earlier (62). Some of the salient features observed were as follows. The activation enthalpies in CTAB microemulsion were lower than for the corresponding micelles (table 2), and the value of ΔH^\ddagger for both nucleophiles were equal in CTAB micelles but not in M.E.. Product analysis showed that, in the case of hydroxide, the actual nucleophile was the butoxide ion. In fact, no monoanion product was observed, a 100% yield of the ester being obtained (equation 5).



The diphenyl phosphate ester is located entirely in the micelle or microdrop. The diethyl ester is partitioned between the aqueous and micellar

Table 2. Comparison of Activation Enthalpies For the Reaction of OH^- and F^- with PhP in CTAB micelles and microemulsion (vide text).

| Nucleophile | ΔH^\ddagger (kcal mol ⁻¹) | |
|-------------|---|-------------------|
| | micelle ^a | M.E. ^b |
| fluoride | 14 | 10 |
| hydroxide | 14 | 8 |

a. Aqueous CTAB micelles (CMC \approx 2.5mM)

b. CTAB/hexadecane/1-butanol microemulsion, 60% water, 10% oil initial (see reference 21).

psuedophases, but is located entirely in the M.E. microdroplet. We have also shown that comparisons are best made between charged and uncharged micelles or microdrops rather than between solution and organize or between different organizes. The results clearly show that while the ester may be entirely solubilized in the microdroplet, its relative location can vary, thus affecting the rate constant. By this method, the effective surface potential in CTAB micelles (slightly above the CMC) is determined to be about 130 mV, compared with values of about 30-60 mV for CTAB microemulsion. This is reasonable since dilution by alcohol cosurfactant should lower the surface charge density (σ) of the microdroplet relative to the micelle. Values of σ calculated from values of α , z_2 and r (vide supra) are consistent with this view.

Since the nucleophile (Y) is aqueous, its initial actual concentration in the M.E. should be given by $[Y]/(1-\phi)$, where $[Y]$ is the overall concentration. Thus, the second order rate constant k_2 calculated by dividing the observed psuedo-first order rate constant by $[Y]$ does not properly reflect the intrinsic (surface) rate constant. We therefore define a phase volume corrected rate constant $k_2\phi$ given by equation 6.

$$k_2\phi = k_2(1-\phi)$$

(6)

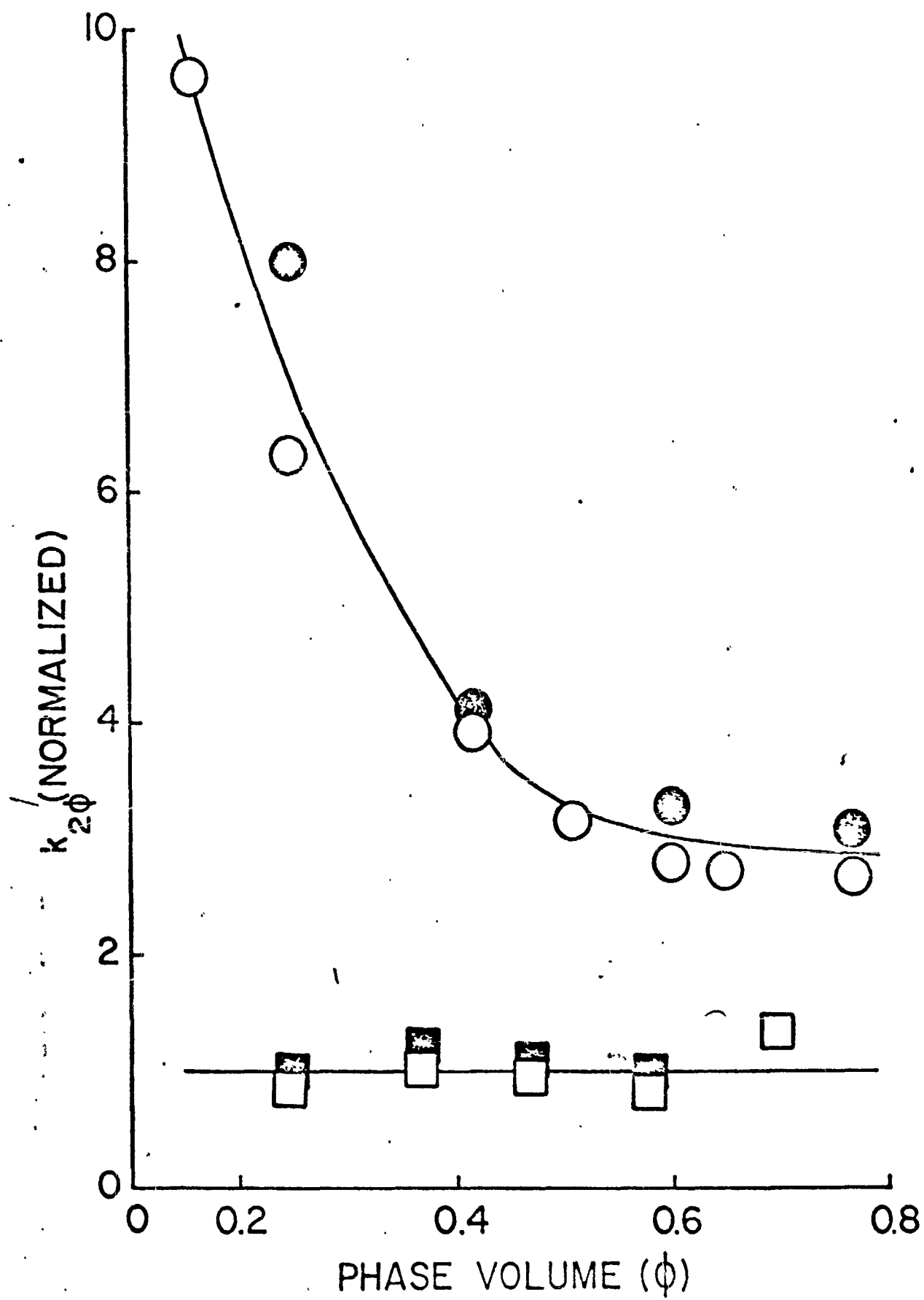
A plot of these rate constants as a function of ϕ for the reaction of PhP with both fluoride and hydroxide is shown in figure 7. Three features are immediately evident. First, the (normalized) results are the same for both nucleophiles. Second, $k_{2\phi}$ does not vary with ϕ in the nonionic M.E.. This is quite reasonable since no major structural changes upon dilution are expected (42). Third, the value of $k_{2\phi}$ increases with increasing dilution for the cationic M.E.. In light of the variation of α with ϕ , this is ascribed to an increased degree of dissociation and thus an increased surface potential with decreasing ϕ .

All evidence to date indicates that, providing solute locations are similar, the intrinsic properties (rate constants, equilibrium constants, quantum yields) are the same in all microemulsions with similar compositions (22,63,64). Therefore, we define an effective surface potential (ψ_ϕ) by equation 7, where e is the electronic charge.

$$k_{2\phi}(\text{CTAB})/k_{2\phi}(\text{Brij}) = \exp(e\psi_\phi/kT) \quad (7)$$

A plot of ψ_ϕ vs ϕ is shown in figure 8. It may be noted that a value of $\psi = 36\text{mV}$ obtained from an indicator pK measurement in the CTAB microemulsion (64) at $\phi = 0.4$ falls on the same curve.

Using this effective surface potential (ESP) model, we have attempted to use the values of ψ_ϕ to determine values of α which can be compared with those obtained from the transport studies (IIA). Again, we have employed the simplest possible model treating the microdroplet and free counterion as a simple electrolyte and the charged surface as a flat plate. An analytical solution of the Poission-Boltzman equation (which does not appear to have been previously published for this specific case) may then be obtained and solved



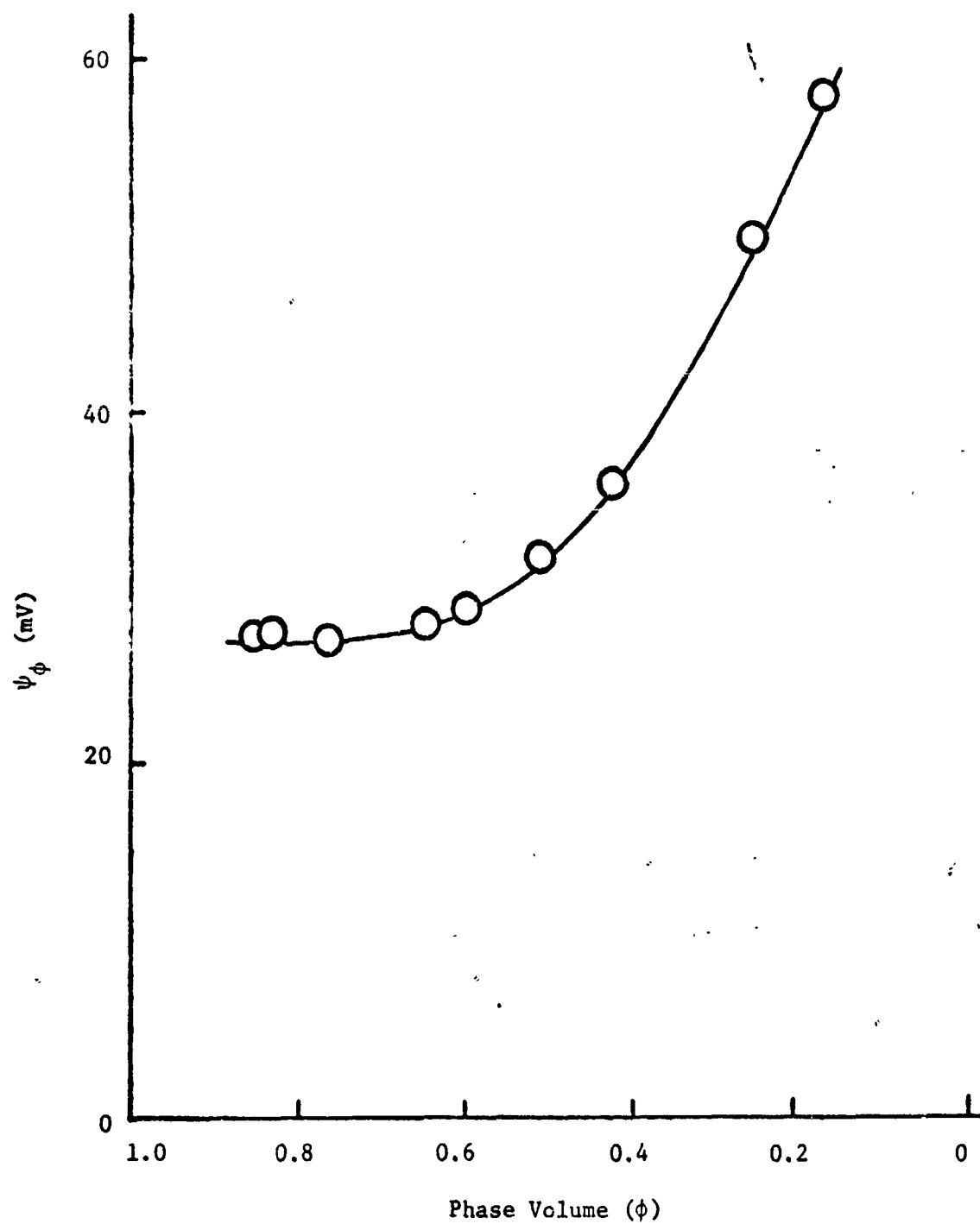


Figure 8. Effective surface potential vs phase volume, from equation 7. (vide text).

for α (equation 3).

$$\alpha = 2(4\pi r^2/ez_2)^2 c \epsilon RT [\exp(e\psi/kT - 1)] \quad (8)$$

Here, all symbols have their previous meaning, and C and ϵ are the total (overall) surfactant concentration and continuous phase permittivity, respectively. Values of α from both the kinetic and conductivity measurements are shown in figure 9. At this point, all that can be said is that the results at least indicate a reasonable degree of consistency between the kinetic and conductivity data. Quite aside from the very simple models employed, the uncertainty in α due only to the uncertainty in the measured parameters is $\pm 10\%$ for the conductivity α 's and $\pm 40\%$ for the kinetic α 's. However, we are encouraged by the present results to move on to the next generation of experiments and calculations in our attempt to develop and test the ESP and other quantitative models (vide infra) for reactions at the microdroplet interface.

It should be noted that the kinetic data in mixed ionic/nonionic (CTAB/BRIJ) microemulsions indicate that mixed microdroplets (analogous to mixed micelles) do form, thus providing continuous control of surface charge.

We have also performed some preliminary investigations into the effect of surface bound nucleophiles on the reaction. By choosing a nucleophile whose active form is pH dependent, we can also investigate surface effects since we have shown that the measurement and interpretation of pH and pK data in microemulsions is not straightforward (64). We have chosen the 1-n-alkyl-3(hydroximinomethyl) pyridinium ion since the anion is known to react with phosphate esters, and the longer chain derivatives form reactive micelles (65). Since the solution must be alkaline (the pK_a of the aldoxime is about

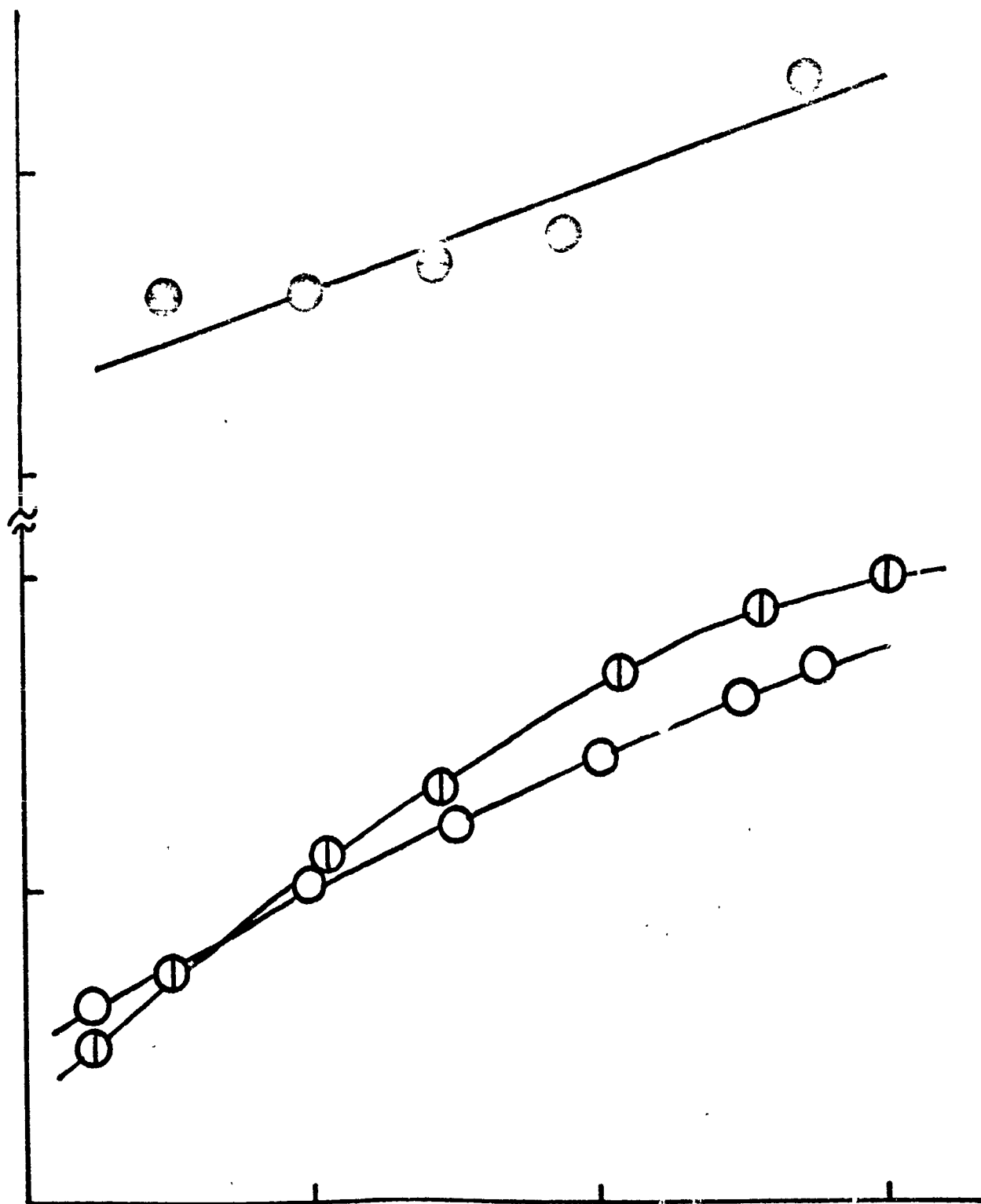


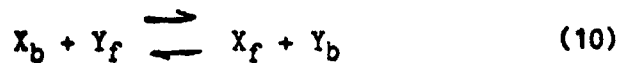
Figure 9. Degree of dissociation (α) vs composition. (a) CTAB microemulsion, conductance data (equation 4); (b) SCS microemulsion, conductance data (equation 4); (c) CTAB microemulsion, kinetic data (equation 8).

9.2), both hydroxide and the aldoxime anion (A) will react. Thus, the observed psuedo first order rate constant k_1 will be given by equation 9.

$$\begin{aligned} k_1 &= k_2(\text{OH}) + k_2'(\text{A}) \\ &= k_2 K_w / (\text{H}^+) + k_2' K_a (\text{AH})_0 / [K_a + (\text{H}^+)] \quad (9) \end{aligned}$$

Here, K_w , K_a and $(\text{AH})_0$ are the ionization constants of water and the aldoxime, and the total concentration of aldoxime, respectively. To insure that all the aldoximate nucleophile was surface bound, the cetyl derivative was used. At $\text{pH} > 10$, $K_a \gg (\text{H}^+)$ and all of the aldoxime is in the anionic form. Under these conditions, a linear plot of k_1 vs $(\text{AH})_0$ is obtained as shown in figure 10. From the slope $k_2' = 0.57 \text{ M}^{-1}\text{s}^{-1}$, while k_2 (determined independently) = $0.18 \text{ M}^{-1}\text{s}^{-1}$. Measurements were also performed at a fixed aldoxime concentration using buffers of varying pH. From these data, we obtain $k_2 = 0.1 \text{ M}^{-1}\text{s}^{-1}$, $k_2' = 0.3 \text{ M}^{-1}\text{s}^{-1}$, and $\text{p}K_a = 9.1$.

C. Ion Exchange Model. In recent years, a psuedophase ion exchange (IE) model has been applied to reactions between substrates in micelles and aqueous nucleophiles (66). The model has had a number of successes and a few partial failures (67). The binding of counterions and coions is treated from the point of view of an ion exchange equilibrium (equation 10),



where X and Y represent the counterion and coion (e.g. nucleophile), and the subscripts b and f represent bound and free. Here, the surface is the region in which the bound ions reside, presumably the Stern layer. Neglecting

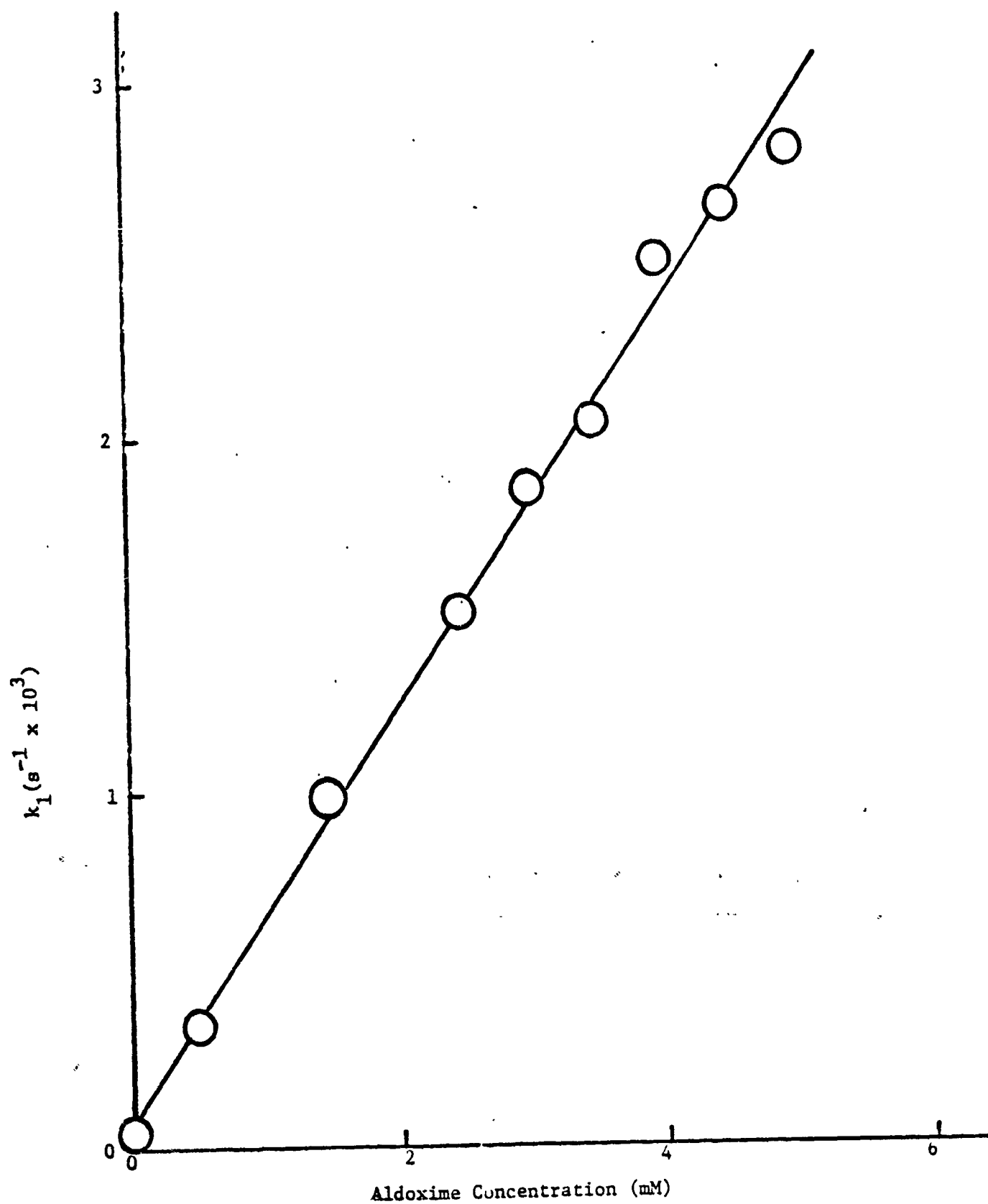


Figure 10. Pseudo first order rate constant as a function of the concentration of 1-hexadecyl-3-pyridinium aldoxime iodide in a CTAB/1-butanol/hexadecane (10% initial) microemulsion at $\tau_{comp} = 0.4$.

activity coefficients, the ion exchange constant (K_{IE}) is given by equation 11, where the concentrations refer to actual (not

$$K_{IE} = (X_f)(Y_b)/(X_b)(Y_f) \quad (11)$$

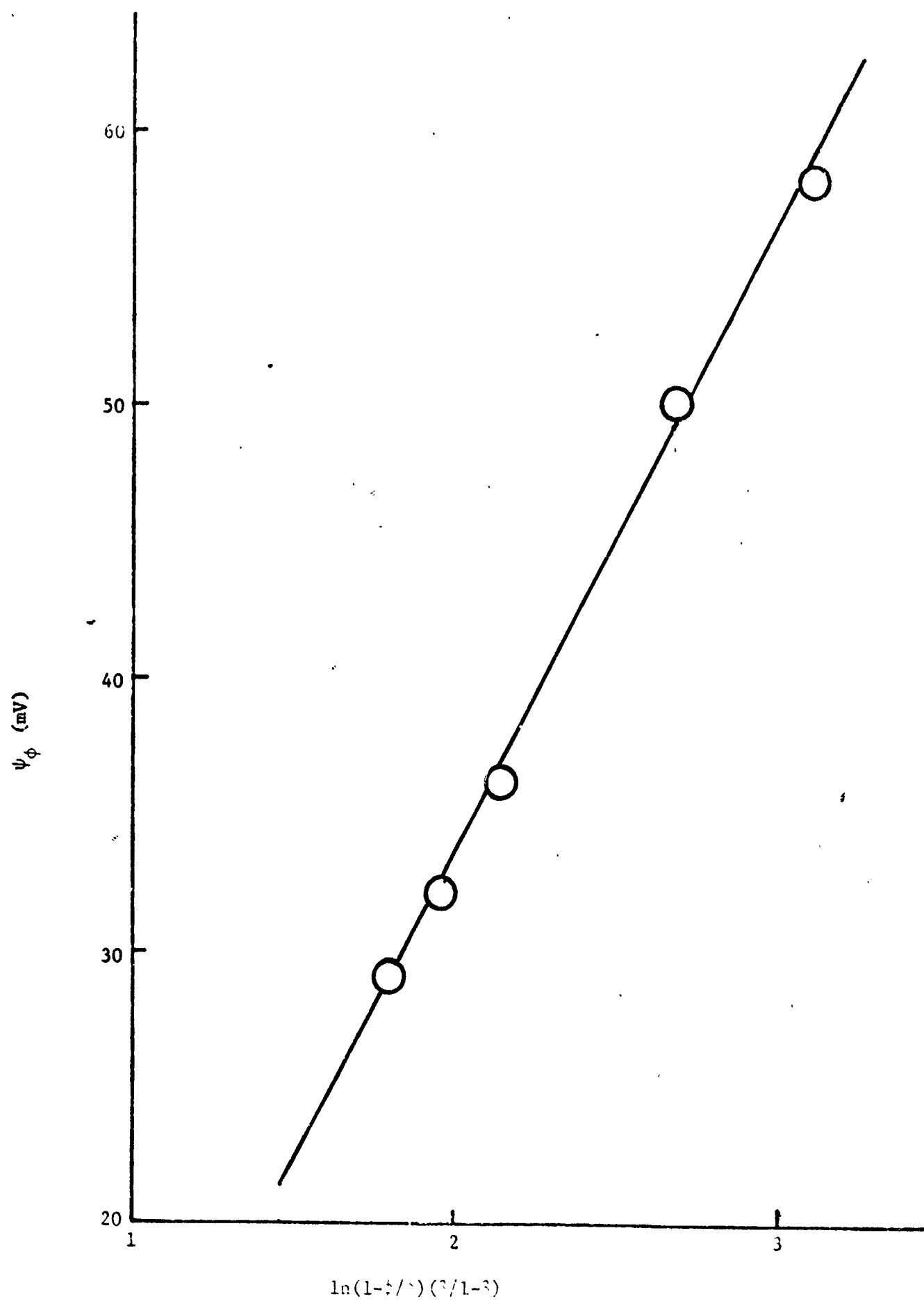
overall) concentrations. It may then be shown that the ratio of phase volume corrected rate constants in ionic and nonionic (e.g. CTAB and Brij) microemulsions is given by

$$k_{2\phi}^{\text{ionic}}/k_{2\phi}^{\text{nonionic}} = (r/3s)(1-\phi/\phi)(K_\phi/1+K_\phi), \quad (12)$$

where s is the thickness of the Stern layer and $K_\phi = K_{IE}^3/(1-\beta)$. The fraction of bound counterion $\beta = 1 - \alpha$. If $K_\phi < 1$, and replacing the ratio $k_{2\phi}^{\text{ionic}}/k_{2\phi}^{\text{nonionic}}$ by $\exp(e\psi/kT)$, equation (12) may be written as

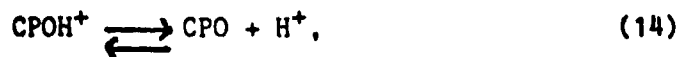
$$\psi_\phi = kT/e \ln(1-\phi/\phi)(\beta/1-\beta) + kT/e \ln(K_{IE}r/3s) \quad (13)$$

Under these conditions, a plot of ψ_ϕ vs. $\ln(1-\phi)\beta/(1-\beta)\phi$ should be a straight line with a slope of 26 mV at 25°C. A plot of data for the reaction of PhP with hydroxide and fluoride, using values of β from the conductivity measurements, is given in figure 11. The slope is 23 mV, and using the polarographic radius of 34Å and assuming $s = 2\text{Å}$, $K_{IE} = 0.1$. This may be compared with values of K_{IE} for exchange between hydroxide and bromide counterion in CTAB micelles of 0.08 (66a) and 0.05 (66d). Here, $K_\phi < 1$ (but not $\ll 1$), and an iteration of the data yields $K_{IE} = .08$. The important point is that the data also fit the IE model. It should be noted that, in contrast to the ESP model, the IE predicts that two different nucleophiles should have



different values of ψ_ϕ since they should have different values of K_{IE} . However, hydroxide and fluoride exhibit very similar ion-exchange behavior, and to make a more definitive test a more hydrophobic ion with a higher value of k_{IE} , such as cyanide, is needed (66b).

This model should also apply to indicator equilibria in the aqueous phase. For example, 1-methyl-4-cyanopyridinium eximate (CPO) has been used as an indicator of environment because of large solvent effects on the wavelength of its intramolecular charge-transfer absorption bands (68). It undergoes the acid-base equilibrium



with an aqueous pK_a of 4.61. Using oxalate buffer in a SCS microemulsion, the parameter $K = (\text{CPOH}^+)_{\text{drop}}/(\text{CPOH}^+)_{\text{aq}}$ may be measured, where the concentrations here refer to overall values. Based on the IE model,

$$K_B = K_{IE} / (1-\delta). \quad (15)$$

an essentially constant value of $K_{IE} = 1.1 \pm 0.2$ is obtained, as shown by the data in table 3.

TABLE 3. CPO indicator equilibrium measurements in an anionic SCS microemulsion (vide test).

| ϕ^a | β^b | K_3^c | K_{IE}^d | \bar{K}_{IE}^e |
|----------|-----------|---------|------------|------------------|
| 0.70 | .93 | 11.3 | 0.9 | 2.1 |
| 0.52 | .87 | 7.9 | 1.2 | 3.0 |
| 0.40 | .83 | 5.6 | 1.1 | 3.0 |
| 0.35 | .82 | 6.2 | 1.4 | 3.7 |
| 0.24 | .80 | 4.9 | 1.2 | 3.2 |
| 0.21 | .80 | 4.2 | 1.1 | 2.8 |

- a. Compositional phase volume for the SCS/1-pentanol mineral oil (21% initial) system (ref. 12).
- b. From conductivity measurements.
- c. Using oxalate buffer (mono and dianion).
- d. Using pH of aqueous buffer. $K_{IE} = 1.1 \pm 0.2$ (ave.)
- e. Using \bar{pH} values (see ref. 64). $\bar{K}_{IE} = 3.0 \pm 0.5$ (ave.)

D. Other Studies: We have initiated a number of reaction studies designed to further probe the behavior of solutes in microemulsions and to explore the range of reactions which can be profitably studied in this medium. There have been very few attempts to investigate the application of microemulsions to the study of inorganic reactions in microemulsions (22). We have performed some further experiments dealing with the formation of metalloporphyrines and the interaction of metal ions with ligands in the microdroplet interphase region (68). The two most interesting observations were the formation of complexes in the surface and, perhaps most striking, the pronounced effect of the nature of the oil phase. For example, the kinetics of the quinoline-promoted incorporation of copper (II) ion by tetraphenylporphine has been examined in a mineral oil in water microemulsions stabilized by SCS and 1-pentanol. A first order dependence of the rate on the quinoline concentration is observed, as compared with a second order dependence in a similar benzene in water microemulsion. The nature of the oil also has a significant effect on the electrochemical reduction of Cu (II), the half-wave potential ($E_{1/2}$) being about 900 mV more negative in the mineral oil microemulsion. The addition of quinoline causes a positive shift in $E_{1/2}$, which we have ascribed to the formation of a four coordinate Cu(I) surface complex. Although aqueous inorganic ions are normally repelled by a microdroplet interface of the same charge, we have found that Cd(II) ion is bound to the droplet in a cationic CTAB microemulsion. We have interpreted this behavior as arising from the formation of anionic species such as CdBr_4^{2-} in the Stern layer. This conclusion is consistent with the results of a study of Cu(II) incorporation by porphyrin in a W/O type microemulsion (69).

We have also begun to explore reactions between inorganic redox reagents and organic substrates. Permanganate and hypochlorite oxidations can be carried out quite effectively. However, the alcohol cosurfactant is also

oxidized. This can be slowed down but not eliminated in anionic systems. Dichromate on the other hand does not oxidize the cosurfactant, but is also not effective with regard to the substrate. However, reducing agents such as borohydride and cyanoborohydride do not react with any of the microemulsion components but do react with typical substrates. For example, we have found that a reasonably rapid reaction takes place between borohydride and monochlorodiethyl sulfide and between cyanoborohydride and p-nitrophenyl alkylketone in a CTAB microemulsion. This illustrates both the already realizable type of reactions, as well as the potential of microemulsions for the utilization of more vigorous redox reagents if other, more stable, cosurfactants can be employed. Certainly, other cosurfactants have been successfully employed, such as acids and amines, and more recently alkoxyethanols, phenol, amine oxides, hexamethylphosphoramide, ethylene oxides and hydroxylamines (70).

We have also begun to explore the reaction of phosphate ester in W/O and surfactant microemulsion phases. The preliminary results indicate discontinuities in rate constants which appear to correlate with similar discontinuities in conductivity and component activity measurements. Various other thermodynamic and structural characterization investigations are currently in progress.

In this section are summarized some of the results and conclusions of the study. There are only meant to be used for quick reference and do not necessarily represent all of the work performed. For more complete details, the body of the report and papers listed in the bibliography should be consulted.

1. Criteria for distinguishing between free and bound electroactive solutes in both ionic and nonionic microemulsions have been established.
2. The conductivity and diffusion coefficient of ionic species in O/W microemulsions can be predicted from the phase volume and the value in water.
3. Droplet radii in ionic O/W microemulsions can be determined from the polarographically measured diffusion coefficient of droplet-bound electroactive solutes.
4. Droplets in nonionic O/W microemulsions exhibit percolation phenomena at phase volumes > 0.10 .
5. A simple model has been applied to conductivity data in ionic O/W microemulsions. Combined with droplet diameter measurements, values of the degree of counterion dissociation can be obtained.
6. Phosphate esters which are partitioned between the aggregate and water in aqueous micelles are completely solubilized in the oil phase in microemulsions.
7. Effective surface potentials can be obtained for ionic systems by comparing rate constants (e.g. for phosphate ester-nucleophile reactions) with those in comparable nonionic microemulsions. These numbers are in good agreement with values obtained by other methods (e.g. $-pK_a$ measurements).
8. Reaction rates between oil solute phosphate ester and anionic nucleophile in cationic microemulsion increase with increasing water content due to an increase in the degree of counterion dissociation (in contrast to aqueous micelles).

9. An ion-exchange model for ionic microemulsions has been developed. This model fits the data for the reaction of ester with anionic nucleophile in a cationic microemulsion, and acid-base indicator equilibrium data in an anionic microemulsion.
10. Surface-bound aldoxime anion reacts with phosphate ester in cationic microemulsion. The effective pKa of the aldoxime in microemulsion is comparable to that in water, and the rate constant for aldoximate is about three times that of hydroxide (butoxide) in a CTAB/butanol/hexadecane system.
11. Inorganic ions can complex with stern layer counterions due to their high effective concentration, thereby effectively binding to drops of the same charge.
12. The nature of the oil phase in an anionic microemulsion has a dramatic effect on the reduction potential of Cu(II) ion. A change from benzene to mineral oil causes a shift of about -0.9 volts.
13. Barohydride can be stabilized in a cationic O/W microemulsion at $\text{pH} \geq 11$.
14. Monochlorethyl ethyl sulfide reacts with borohydride at a reasonable rate in cationic microemulsion to produce diethyl sulfide.

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